Scaling Models for the Refractive Index of HFC 134a and HFC 143a on the Coexistence Curve

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Abstract

A scaling form for the refractive index n is investigated in the work. It based on the scaling theory (ST) and experimental data on n_l,n_g,T – data Yata [1,2] along the coexistence curve (CC) including a wide region around the critical point of HFC 134a and HFC 143a. A methodical part deals with an equation $n_{l,g}$ (T) that is a combination of two properties, the order parameter f_s and the diameter of CC f_d . It is accepted that the properties, Y = (f_s,f_d,), have a scaling part, Y_{scal}, and a regular one, Y_r. The form of Y_{scal} has followed to the scaling theory (ST), depended on the relative distance τ from T_c and parameters (critical exponents (α , β ,(Δ_i)) and amplitudes, (B_{si}), (B_{di})).

A routine and some criterions are elaborated for the task: to determine parameters of Y with the help of n_l,n_g,T – data. The scaling function $\psi_{l,g}$.is used to analyze Y. With the help of the routine numerical parameters of $n_{l(}\tau)$ and $n_{g(}\tau)$ are calculated. They represent reliable experimental points in a region from 300 K up to T_c. The relations represented reliable measured points including new data in limits of experimental errors and can be helpful to calculate densities on CC in a wide region of the critical point, $0.00003<\tau<0.2$. The relations, $\rho_{l(}T)$,$\rho_{g(}T)$, include effective values of critical exponents, α , β . A comparison has shown that there is a

satisfy agreement the values with exponents, α, β, those are used in scaling equations, $\rho_l(T)$, $\rho_g(T)$.

Keywords: HFC 134a; HFC 143a; Thermodynamic properties; Scaling equation; Refractive index; Density of liquid, Density of vapor; Coexisting curve.

1. Introduction

Due to ST the properties on CC, $\rho_l(T)$,$\rho_g(T)$, can be represent with the help of the order parameter f_s and the diameter of CC f_d [3,4] in some region of T_c.

$$f_s=(\rho_l - \rho_g)(2\rho_c)^{-1}=B_{s0}\tau^{\beta} + B_{s1}\tau^{\beta+\Delta 1} + B_{s2}\tau^{\beta+\Delta 2}, \quad (1.1)$$

$$f_d=(\rho_l + \rho_g)(2\rho_c)^{-1} - 1= B_{d0}\tau^{1-\alpha}{}_{+} B_{d1}\tau^{1-\alpha+\Delta 1} + B_{d2}\tau^{1-\alpha+\Delta 2}. \quad (1.2)$$

The first addend in (1.1) (1.2) represents the asymptotic component, the second and the third terms give non asymptotic components (the first and the second correction terms with correction exponents Δ_1 and Δ_2.

Analytic equations, $\rho_l(T)$,$\rho_g(T)$, can be determined with the help of known (1.1,1.2) as

$$\rho_l = (f_d + f_s + 1)\,\rho_c\,, \qquad \rho_g = (f_d - f_s + 1)\,\rho_c\,. \quad (1.3)$$

Equations (1.1.,1.2) are named Model 1, they can approximate experimental data in a working interval $\Delta\,\tau_w \approx$ 0.15 of T_c ($T_c > T > T_w$, $\Delta\tau_w = 1 - T_w/T_c$) for different substances. RMS deviations, S_g,S_l, are small and no systematic deviations are realized. Our practice showed if T_w decreases and $\Delta\,\tau_w > 0.1$ then RMS deviations, S_g,S_l, increase and remarkable systematic errors appear. A combined model named Model 2 is proposed for the case in [3,4].

We have decided to choose an analogous form for representation of $n_{l,g}(\tau)$ equation.

2. Models, criterions and routines

To represent n_l,n_g,T – data in $\Delta\tau_w > 0.1$ we have taken Model 2 adopted to $n_{l,g}(\tau)$

$$f_s=(n_l - n_g)(2n_c)^{-1} = B_{s0}\tau^{\beta} + B_{s1}\tau^{\beta+\Delta 1} + B_{s2}\tau^{\beta+\Delta 2} + B_{s3}\tau^{2} + B_{s4}\tau^{3}\,, \quad (2.1)$$

$$f_d=(n_l + n_g)(2n_c)^{-1} = B_{d0}\tau^{1-\alpha}{}_{+} B_{d1}\tau^{1-\alpha+\Delta 1} + B_{d2}\tau^{1-\alpha+\Delta 2} + B_{d3}\tau^{2} + B_{d4}\tau^{3}. \quad (2.2)$$

Analytic equations, $\rho_l(T)$,$\rho_g(T)$, can be determined with the help of known (2.1,2.2) as

$$\rho_l = (f_d + f_s + 1)\,\rho_c\,, \qquad \rho_g = (f_d - f_s + 1)\,\rho_c\,. \tag{2.3}$$

Two regular terms in (2.1,2.2) are involved with the aim to reduce possible systematic deviations mentioned for Model 1 under τ_w >0.1. Model 2 is to have the following characteristics: 1) it approximates n_l, n_g, T – data in $\Delta\tau_w$ >0.1 with acceptable RMS deviations, S_g, S_l, 2) at the same time its scaling part (it can be consider as Model 1) delivers acceptable RMS deviations, S_g, S_l, for points in $\Delta\tau_w$ = 0.1 when Model 1 is used to calculate deviations of ρ_l, ρ_g, T – data in $\Delta\tau_w$ =0.1. In the case the regular terms play a role of correction addends: S_l(Model 1) ≈ S_l(Model 2) and S_g(Model 1) ≈ S_g(Model 2).

An approximation quality of Model 2 is characterized by individual and RMS deviations of experimental ($n_{g\,exp\,k}, n_{l\,exp\,k}$) values from those calculated with equations (2.3)

$$\delta\rho_{gk} = 100\,(\rho_{g\,exp\,k} - \rho_{gk})/\,\rho_{gk}\,, \qquad S_g = (\Sigma\delta\rho_{gk}^{\,2}\,/\,N)^{\,0.5},$$

$$\delta\rho_{li} = 100\,(\rho_{l\,exp\,k} - \rho_{lk})/\,\rho_{lk}\,, \qquad S_l = (\Sigma\delta\rho_{lk}^{\,2}\,/\,N)^{\,0.5}, \tag{2.4}$$

Model 2 can be considered as $Y = (f_s, f_d,)$ that includes parameters, $D = (\rho_c, T_c, \alpha\,, \beta\,, (\Delta_i))$, and coefficients, $C = ((B_{si}),(B_{di}))$. Values of C are to be determined by an approximation of the input data set $(Y_{exp\,k}, \tau_k)$. If D are considered as the parameters fixed and known (taken from literature sources) then $Y = f(D, C, \tau)$ is a linear function of C. In the case it is possible to calculate C using a weighted least-squares analysis (LSQA) and a single criterion – a minim of the functional $\Phi(C,D)$

$$\Phi(C,D) = \sum_{k=1}^{N} w_k\,(Y_{exp\,k} - f(D,C,\tau_k))^2/N = min. \tag{2.5}$$

Routine 1 is elaborated for C calculation and has the following steps: i) to consider D as the parameters fixed and to take from literature sources; ii) to form a sum of squares, $\Phi(C,D)$, for the input data set; iii) to calculate a realization C, that is numerical values of C, using a weighted least-squares analysis (LSQA) and a single criterion – a minim of $\Phi(C,D)$; iiii) to estimate a quality of the approximation that is to calculate individual and RMS deviations .

Routine 1 was used and gave an opportunity to examine a group of realizations ($Y = f(D_j, C_j, \tau)$, $j = 1\ldots K$). Criterion (1.6) shows that $\Phi(C,D)$ $S_{l,g}(D)$ are some functions of parameters

D. If Routine 1 is used at the first time then the following numerical values appear: parameters, $D = D_1$, a realization, $C = C_1$, RMS deviations, $S_{l,g}(D_1)$. If one of the parameters D_1 is shifted (for example ρ_c can be shifted on $\Delta\rho_c$ in limits of an experimental estimation $\pm\Delta_{\rho c}$) then Routine 1 can be used at the second time and the second set, $D_2, C_2, S_{l,g}(D_2)$, can be got. Many numerical variants (realizations (C_j)) of Models 1,2 and according deviation sets ($S_{l,g}(D_j)$) were got, among them there were such numerical dependences as $S_{l,g}(n_c), S_{l,g}(T_c)$, $S_{l,g}(\beta)$ in some region of S_l^{min} and S_g^{min}. Our analyses have estimated some general features of the realisations: i) values of S_g and S_l did not coincide ($S_l < S_g$), the global minimal values were found between them (Model 2 has given S_l^{min} =0.01% and S_g^{min} = 0.005% for HFC 134a points related to $\Delta\tau_w$ = 0.25, ii) the leading amplitudes, $B_{s0}, B_{d0,}$ deviated greatly from middle calculated values, B_{s0}, B_{d0}, iii) it was impossible to find a variant C_j that delivered $S_l = S_l^{min}$ and $S_g = S_g^{min}$ at once. The last circumstance was one of the reasons to look for an optimal Models 1,2 ($Y = f(D_{opt}, C_{opt}, \tau)$) with an optimal realization C_{opt} that deliver compromise values of $S_{l,g}(D_{opt})$. It was admitted that the realization $Y = f(D_{opt}, C_{opt}, \tau)$ is optimal when Y deliver RMS deviations those follow to the compromise criterions

$$S_l(D_j) - S_l^{min} < \varepsilon_1, \qquad S_g(D_j) - S_g^{min} < \varepsilon_2, \tag{2.6}$$

where ε_1 and ε_2 – some limits.

Our practice and analysis of realizations, (Y_j), have showed that more criterions have to be involved for the purpose to choose an optimal variant from realizations (Y_j) those satisfied criterions (2.6). One more property is considered in ST and involved in the work: the scaling function $\psi_{l,g}$ that can be expressed in the form

$$\psi_{l,g} = |(n_{l,g} - n_c)(2n_c\tau^{\beta})^{-1}| = |\pm B_{s0} + B_{d0}\tau^{1-\alpha-\beta} \pm B_{s1}\tau^{\Delta 1-\beta} + B_{d1}\tau^{1-\alpha+\Delta 1-\beta} + \ldots|, \tag{2.7}$$

where the upper (plus) sign of terms corresponds to the liquid branch (l), the lower (minus) corresponds to the vapor branch (g) of $\psi_{l,g}$.

Investigations [3,4,5] estimated that the scaling function $\psi_{l,g}$ can be used as an additional criterion. $\psi_{l,g}$ is written in a narrow interval $\tau_w \approx 0.01$ as two terms expression that includes only leading addends with the asymptotic exponents

$$\psi_{l,g} \approx |\pm B_{s0} + B_{d0}\tau^{1-\alpha-\beta}| . \qquad (2.8)$$

A numerical form (2.8) of $\psi_{l,g}$ was found and analysed for several liquids (H_2O,Ne,N_2,HFC 134a, HFC 143a a. o.). Due to (2.8) an optimal variant, $Y = f(D_{opt},C_{opt},\tau)$, is to follow to the next features: i) $\psi_{l,g}$ is symmetric to the amplitude B_{s0} for liquid and vapour branches, ii) the plot of $\psi_{l,g}$ versus $\tau^{1-\alpha-\beta}$ is liner and converge symmetrically to B_{s0}, iii) asymptotic Model 0 as $Y = f(D_{opr},C = B_{s0},B_{d0},\tau)$ can be built, optimal Model 0 is to have a satisfied agreement with experimental points related to $\tau_w \approx 0.01$, RMS deviations, S_l,S_g, are close to criterions (2.6) in the case. An illustration of $\psi_{l,g}$ as a function of $\tau^{1-\alpha-\beta}$ is given in Fig. 1,2. Experimental values of $\psi_{l,g}$ are shown as well as values determined with the help of Models 0,1,2 for HFC 134a. Two methods of parameters D chose were examined for the task. Due to the first one D components are taken as theoretical or experimental values and not varied during a treaty of the input data set. For example the exponents are taken in [2] as theoretical data β=0.325, α =0.1085 and Δ = 0.5 for the densities equations, $\rho_l(T)$,$\rho_g(T)$. We have used the way for (Δ_i) determination and chosen $\Delta_1 = \Delta = 0.5$ and $\Delta_2 = 2\Delta$ as theoretical values. The second method [3 - 6] considers D = (ρ_c,T_c,α , β ,B_{s0},B_{d0}) as fixed parameters for the densities equations, $\rho_l(T)$,$\rho_g(T)$; D is known in a region of possible deviations ($\pm\Delta D$) and the method let us i) shift D in the limits ($\pm\Delta D$) corresponding to some criterions, ii) examine a group (D_j) and choose an optimal variant. We underline that leading amplitudes, B_{s0},B_{d0}, are also included in D and they do not take part in LSQA when amplitudes C are determined. This schema has been accepted in the work.

The middle value of D components and a region of possible deviation ($\pm\Delta_{\rho c}$,$\pm\Delta_{Tc}$,$\pm\Delta_{\beta}$ a.o.) were found among parameters of realization, (Y_j), calculated during the investigation. The start values were chosen: α =0.1085 and β=0.325, T_c = 374.107 ± 0.02 K [1], n_c = 1.08990 [1]. The

characteristics were combined in a group $D_1 = (n_c, T_c, \alpha, \beta, \Delta, B_{s0}, B_{d\,0})$ as a start data. The value β=0.348 ± 0.001 was reported by Yata [1] as an effective exponent got from ρ_l, ρ_g, T – data. The region was also used in Routine 2.

Routine 2 was elaborated using criterions (2.6,2.8). It consisted of several steps: i) to take D_1 as start fixed parameters, ii) to calculate the realization C_1 employing weighted LSQA, iii) to determine the criterions ($S_l, S_g, \psi_{l,g}$) and to analyse them; if the analysis showed that criterions ($S_l, S_g, \psi_{l,g}$) satisfied conditions (2.3,2.4) then the routine was to finish. On opposite site, a new fixed parameter (for example, it was n_c) was to be chosen (n_c was shifted on 0.1 Δ_{nc}), D_2 was formed and treaty was continued (steps ii,iii) to get next realisation C_2. There is an illustration in Fig. 1 of a dependence, $S_l(n_c)$, when n_c is shifted step by step in a region, Δ_{nc}, of S_l^{min}. Routine 2 builds Models 1,2 for HFC 134a when n_c increases from 1.089795 to 1.089805 with the step 0.000001 and the value of S_l changes in the interval 0.021…0.15 %. The dependence shows: if the limit is taken as $\varepsilon_2 \approx 0.01\%$ then n_c lies in the interval 1.089801 $\pm$ 0.000001. A similar dependence is found for $S_g(n_c)$ and $\varepsilon_2 \approx 0.01\%$ has been accepted .

Routine 2 let us get Models 1,2 those had effective parameters, D_{opt}, C_{opt}, and were agree with conditions (2.3,2.4). The routine was used to build Model 1,2 using n_l, n_g, T –points of HFC 134a and HFC 143a in $\tau_w \approx 0.2$. The limits, $\varepsilon_1, \varepsilon_2$, are determined as $\varepsilon_1 = \varepsilon_2 \approx 0.01\%$. Numerical parameters of Model 2 are placed in tables 1,2. Model 2 was fitted to the input data set with acceptable accuracy in the gas and liquid phases. Values of $\psi_{l,g}$ calculated with the parameters (table 1) are placed in Fig. 2,3. There are values determined with the help of Models 0,1 in Fig. 2. The models have used the parameters (Table 1) and represent scaling terms of a combined equation (2.1,2,2). In Fig. 3 there are values determined using Model 2 with the parameters (Table 1). Experimental values of $\psi_{l,g}$ are shown too.

Following approximation characteristics, S_l,S_g,S_l^{min},S_g^{min}, were got: for Model 1 S_l =0.017%, S_g = 0.013%, S_l^{min} = 0.021 %, S_g^{min} = 0.014 %; for Model 2 S_l =0.019, S_g = 0.021%, S_l^{min} = 0.012 %, S_g^{min} = 0.013 %.

Table 1. Parameters of Model 2 for HFC 134a.

n_c	T_c /K	α	β	Δ	
1.089801	374.105	0.1509	0.34942	0.5	
B_{s0}	B_{s1}	B_{s2}	B_{s3}	B_{s4}	
0.1757	0.003521	-0.0369	-0.030079	0.095459	
B_{d0}	B_{d1}	B_{d2}	B_{d3}	B_{d4}	
0.06605	0.011038	0.030092	-0.000207	-0.004037	

Table 2. Parameters of Model 2 for HFC 143a.

n_c	T_c /K	α	β	Δ	
1.09125	345.815	0.22	0.3515	0.5	
B_{s0}	B_{s1}	B_{s2}	B_{s3}	B_{s4}	
0.1761	0.006851	-0.066169	0.053325	0.148388	
B_{d0}	B_{d1}	B_{d2}	B_{d3}	B_{d4}	
0.0066	0.250177	-0.326997	0.0673	0.131136	

There is an illustration in Fig. 4 of a dependence, S_l (T_c), for Modes 1,2 when T_c is shifted step by step in the interval Δ_{Tc} = 374.10…374.12 K including the point with S_l^{min}. Routine 2 let us use the step 0.0005 …0.001 K and estimate that S_l changes in the interval 0.021…0.35 %. (Model 1) and 0.012…0.033 % (Model 2). The dependence shows: if the limit is taken as $\varepsilon_2 \approx$ 0.01% then i) T_c can be chosen as T_c = 374.105$\pm$ 0.001 K and ii) Models 1,2 will have the following criterions of approximation: S_l = 0.021…0.031 for Model 1, S_l = 0.05…0.021% for Model 2. A comparison shows that Models 1,2 have similar RMS deviations at T_c = 374.105 K.

The equalities, S_l(Model 1) ≈ S_l(Model 2), S_g(Model 1) ≈ S_g(Model 2), mean that the scaling part plays the leading role and the influence of the regular part is small in optimal variant of Model 2.

4. Conclusion

The analysis of realizations, an optimal variant of Model 2 and results of a comparison with the data [1,2] allows us to make an output that the structure of Model 2 can be useful to approximate experimental data on a line of the phase equilibrium including a broad neighborhood of the critical point. Numerical variants of $n_l(T), n_g(T)$ for HFC134a represent experimental data in the region, $0.00003<\tau<0.2$, with satisfy RMS deviations: for Model 1 S_l =0.017%, S_g = 0.013%; for Model 2 S_l =0.019%, S_g = 0.021%. The Models can be used to determine accurate $\rho_l, \rho_g T$ – data including asymptotic region of the critical point where traditional methods have a low accuracy. Effective values of critical characteristics, $n_c, T_c, \alpha, \beta, B_{s0}, B_{d\,0}$, are interesting data for problems of ST.

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List of symbols

T = temperature

P = pressure

ρ = density

P_s = saturated pressure

g, l, c = indexes to mark the vapor and liquid phases on CC and a value in the critical point

$\alpha, \beta, (\Delta_i)$ = critical exponents

$\tau = 1 - T/T_c$ = relative distance of temperature from T_c,

(B_{si}), (B_{di}), (B_{pi}) = amplitudes

$\delta\rho_{g\,k}, \delta\rho_{l\,k}$ = relative deviations of the vapour and liquid densities in k – point

$\rho_{g\,exp\,k}, \rho_{l\,exp\,k}$ = experimental values of the the densities

$\rho_{g\,k}, \rho_{l\,k}$ = values of the vapour and liquid densities calculated with (1.4)

N = the number of points in the input data set

S_g,S_l = relative RMS deviations of vapour and liquid densities.

w_k = weight coefficient for k – point

References

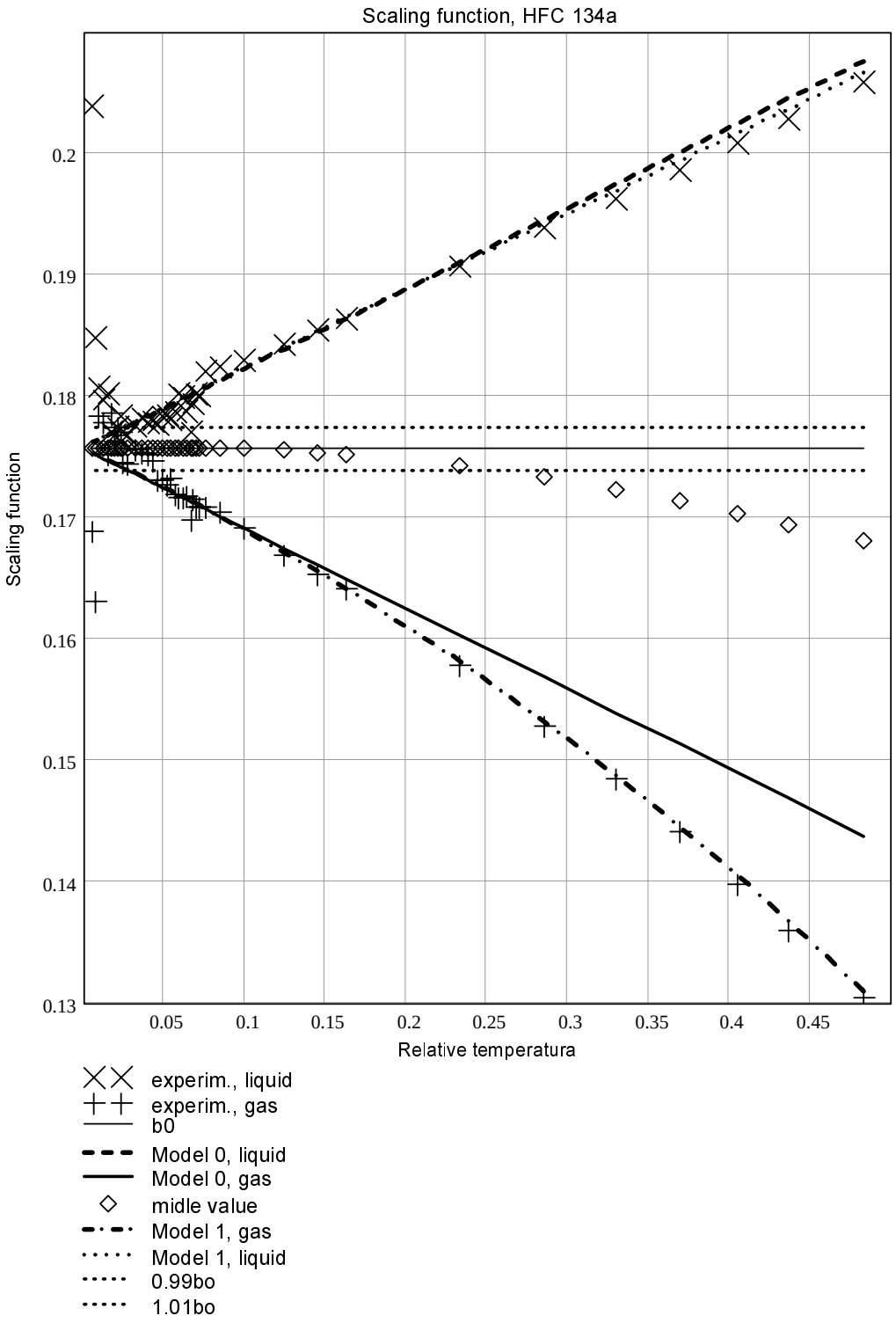
1. J. Yata, in Proc. of the 1st Workshop on thermochemical, thermodynamic and transport properties of halogenated hydrocarbons and mixtures, (Pisa, Italy), (1999) 120-124.
2. J. Yata, Hori M, Kohno K. and Minamiyama T. *High Temperatures – High Pressures* , **17**: (1997) 65-72.
3. E.E. Ustjuzhanin, Reutov B.F., Kusubov K.B. In Proc. of Fourteenth Symposium on Thermophysical Properties, (Boulder, Colorado, USA, June 25-30) (2000).
4. E.E. Ustjuzhanin, J. Yata, B. Reutov, B. Grigoriev, J. Magee In Proc. of 16-th European Conference on Thermophysical Properties (Imperial College, London, 1-4 Sept) (2002).
5. E.T. Shimanskaya, Yu.I. Shimansky and A.V. Oleinikova, Int. J. Thermophys. 17, (1996) 641 – 649.
6. V.A. Rabinovich, Yu.E. Sheludiak, Thermophys. of High Temperture (rus) V. 33, N4, (1995) 546-552.

Fig. 1. The scaling functions $\psi_{l,g}$ of HFC 134a.
Values are determined from 1) the experimental data, 2) Models 0,1;
$b0$ – leading amplitude B_{s0}; relative temperature – $\tau^{1-\alpha-\beta} = (1 - T/T_c)^{1-\alpha-\beta}$

Fig. 2. The scaling functions $\psi_{l,g}$ of HFC 134a.
Values are determined from 1) the experimental data, 2) Models 2;
$b0$ – leading amplitude B_{s0}; relative temperature – $\tau^{1-\alpha-\beta} = (1 - T/T_c)^{1-\alpha-\beta}$

Fig. 3. The influence of n_c on the criterions S_l for Model 1 and Model 2 of HFC 134a

Fig. 4. The influence of T_c [K] on the criterions S_l for Model 1 and Model 2 of HFC 134a



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$b0$ – leading amplitude B_{s0}; relative temperature – $\tau^{1-\alpha-\beta} = (1 - T/T_c)^{1-\alpha-\beta}$

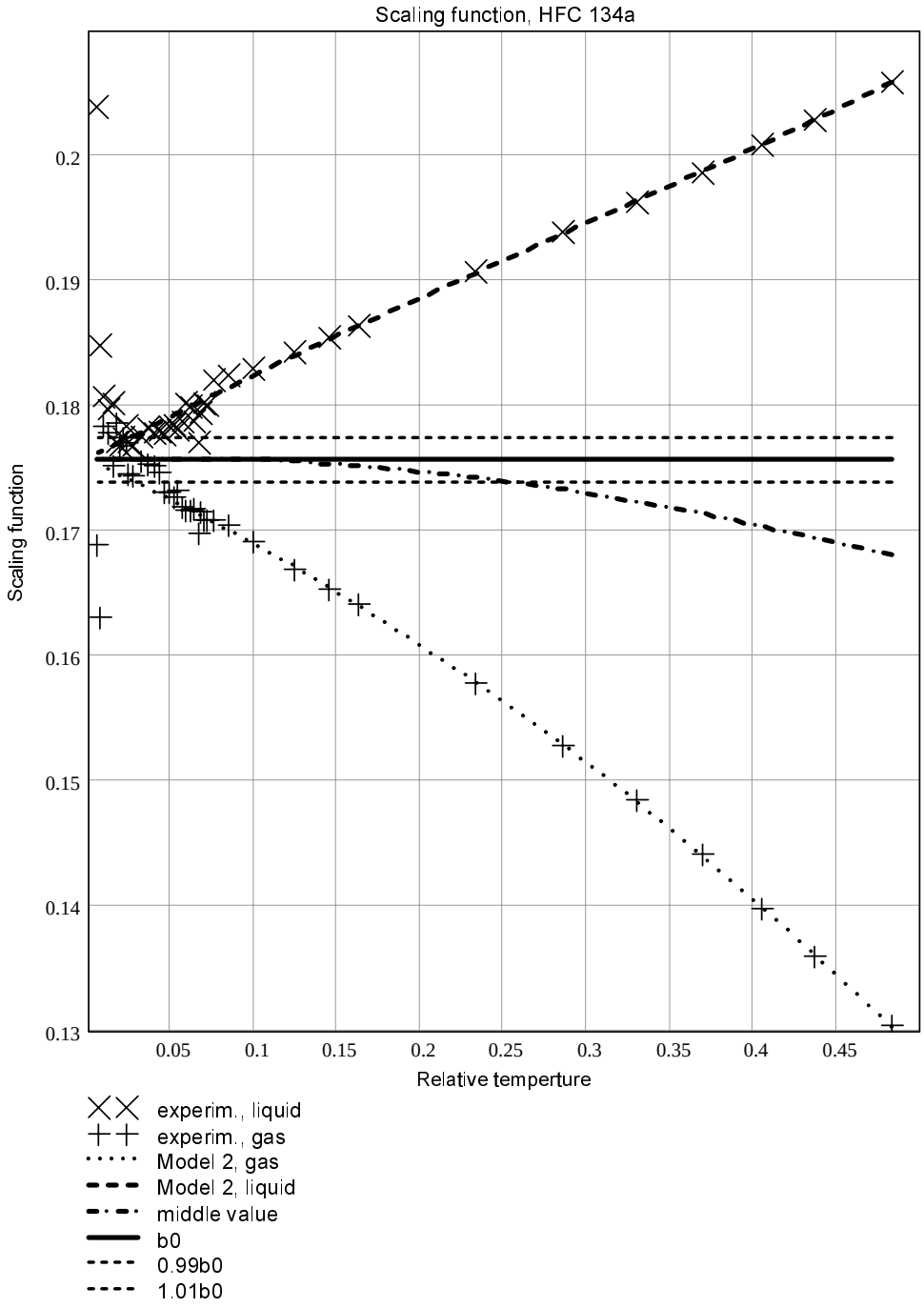

Fig. 2. The scaling functions $\psi_{l,g}$ of HFC 134a.
Values are determined from 1) the experimental data, 2) Models 2;
$b0$ – leading amplitude B_{s0}; relative temperature – $\tau^{1-\alpha-\beta} = (1 - T/T_c)^{1-\alpha-\beta}$

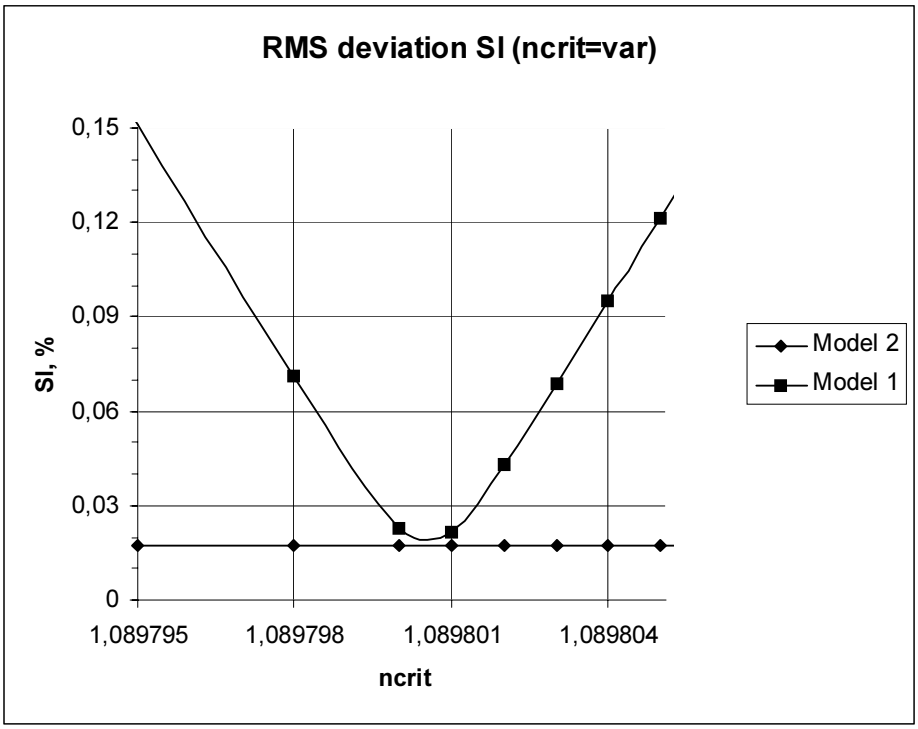
RMS deviation SI (ncrit=var)
0,15
0,12
0,09
0,06
0,03
0
SI, %
1,089795
1,089798
1,089801
1,089804
ncrit
Model 2
Model 1

Fig. 3.

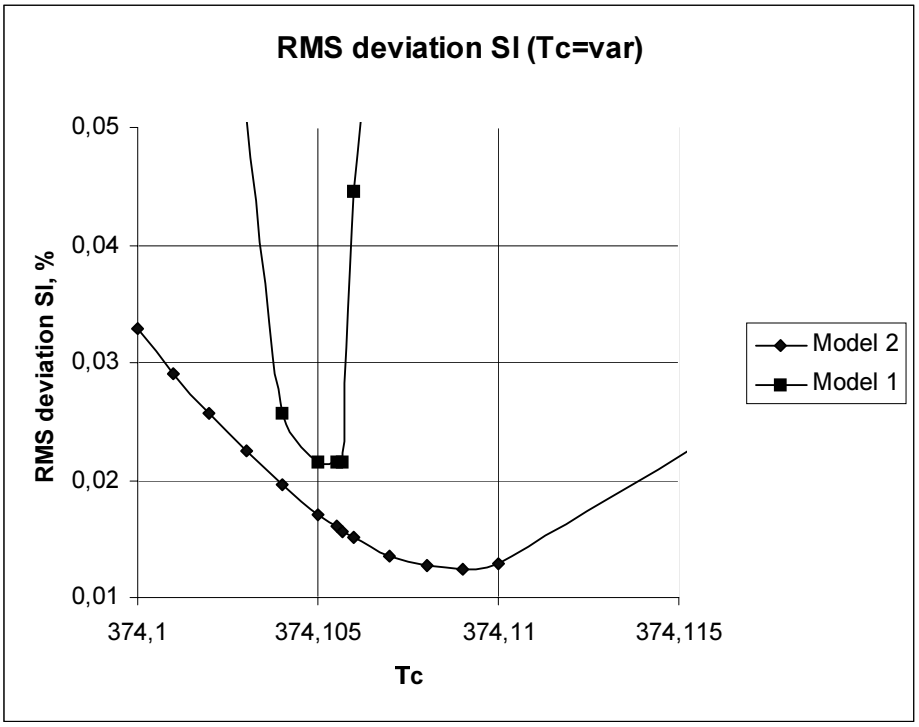

Fig. 4. The influence of T_c on the criterions S_I for Model 1 and Model 2